INDICATORS FOR THE OPTICAL MEASUREMENT OF SULPHUR DIOXIDE GAS

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ABSTRACT

A number of fluorophores were investigated for their suitability to be employed as indicators in SO_2 measurement. Several indicators, including PAH's, 5(and 6) carboxy-4'-5'-dimethyl fluorescein, new fuschin, hydrazine hydrochloride and chloropyridine hydrochloride, showed decrease in the fluorescence intensity with increase in SO_2 concentration. Fluorescence quenching of benzopurpurin by SO_2 is found to be extremely efficient, with a little or no interference from the other toxic gases NH_3 and H_2S. These results are analyzed using Stern-Volmer relation. The finding is considered to be of potential utility for the development of an improved fibre optic SO_2 sensor/probe.

1. INTRODUCTION

Sulphur dioxide (SO_2) is recognized as one of the primary air pollutants, and concentrations of 5 - 10 ppm in air have been recommended as threshold value for human exposure. It is present in stack gases or exit combustion products from industries and automobiles that utilize sulphur containing fuels. Sulphur dioxide is also associated with the widely known "acid rain" phenomenon and with corrosion.

Both off-line and on-line methods for quantitatively measuring SO_2 concentrations are known. The conventional discontinuous methods depend on the spectroscopic measurement of the dye complexes formed by reagents and sulphur dioxide or iodometric titration. Other methods of SO_2 measurement include chemiluminescence[1], potentiometry, chromatography and fluorescence. However, such methods are tedious, time consuming and require expensive instrumentation. Only potentiometric and fluorometric methods can be used for continuous monitoring of SO_2.

Recently, Sharma and Wolfbeis[2] described fluorescence quenching based method for the measurement of SO_2. In this method a fluorophore is employed which is sensitive to SO_2 concentrations. Reduction in the fluorescence intensity due to the presence of SO_2 can be used to quantitatively measure SO_2 concentrations. Potential of this method for on-line application was demonstrated by incorporating the fluorophore in a SO_2 permeable polymer and constructing an optical sensor[3]. Based on Sharma's earlier work[4], these authors further improved the performance of their SO_2 sensor by using two indicators[5] and making use of both the energy transfer and fluorescence quenching simultaneously (this phenomenon which was observed by Sharma in 1980 leads to increased sensitivities, large Stokes' shifts and increased photostability).

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The method of Sharma and Wolfbeis has several advantages over the other existing methods for the measurement of SO_2. However, most of the indicators suggested by these authors absorb in the ultra-violet region of the optical spectra and have small Stokes' losses. The sensors and indicators reported by these authors suffer from severe interferences from several other gases and vapours, such as oxygen, chlorine and hydrogen chloride. Further, the sensitivity and the detection limits offered by these indicators make them unsuitable for use in real-time monitoring applications where very low levels of SO_2 are needed to be measured, such as in the cockpit of the car, in ambient air and inside working facilities of laboratories or industries.

Therefore, there is a need for a rapid, sensitive, selective and reliable method for monitoring SO_2 concentration. In continuation to our work on molecular fluorescence and its diagnostic applications[6-7], we discuss in this paper various fluorophores which are sensitive to sulphur dioxide. A SO_2 selective indicator which can be used to monitor dissolved SO_2 both in liquid or gas mixtures is also reported. Quantitative data on the fluorescence quenching process is reported, and possibilities of exploiting this phenomenon for analytical purposes are discussed.

2. EXPERIMENTAL

Fluorescence spectra of dye solutions in methanol (dried over $CaCl_2$ and doubly distilled) were recorded on a Perkin-Elmer LS 5 spectrofluorimeter which was equipped with a Hamamatsu PMT R928P as detector. All the spectra were recorded in 1 X 1 cm rectangular quartz cells at a room temperature of 22 °C. The concentration of the fluorophore solutions was kept constant at ~15 uM to avoid inner filter effect or self quenching.

2.1. Preparation of SO_2 Solutions

The stock solution of SO_2 in methanol was prepared as reported earlier[2]. The concentration of this solution was determined by iodometric titration. The stock solution was found to be 0.263 M in SO_2. Desired dilutions were made from the stock solution to perform further experiments.

2.2. Choice of Suitable Fluorophores

The following compounds in methanol solution were first studied qualitatively with respect to fluorescence quenching by SO_2: 5(and 6) carboxy-4'-5'-dimethyl fluorescein (CDF), new fuschin, benzopurpurin, nuclear fast red, methylene-n-zinc chloride, thioflavin T, thionine, hydrazine hydrochloride, chloropyridine hydrochloride and a number of PAH,s. Fluorescence quenching by SO_2 was effective in several cases, namely new fuchsin, benzopurpurin, hydrazine hydrochloride, chloropyridine hydrochloride, PAH's and CDF. Other indicators showed either no effect or a slight increase in the fluorescence intensity on addition of 1 mM SO_2 solution. Though all the indicators had favourable longwave spectral properties (except chloropyridine hydrochloride, most of PAH's and hydrazine hydrochloride which has absorption maxima ca. 256 nm and 307 nm, respectively) coupled with large Stokes' shift and good quantum yields, only benzopurpurin (BP) was found to have no interference from the basic gas NH_3 and acidic gas H_2S. However, interference from HCl is there. The fact that it is not a very common situation that a sample contains both HCl and SO_2, and given the favourable spectroscopic and analytical properties, such as large Stokes' shift, sharp emission bands, good quantum yield, good photostability, visible excitation, high sensitivity towards sulphur dioxide and high solubility of benzopurpurin in methanol, made it the most suitable candidate for detailed investigations. Of course, water would not interfere when this dye is incorporated in a hydrophillic material, such as silicone rubber, for instance, when used in a fibre optic sensor.

The choice of methanol as solvent was governed by the fact that it easily dissolved all the dyes investigated, it was available in pure-dry form, and SO_2 and other gases are readily soluble in it.

3. RESULTS AND DISCUSSION

Table 1. Fluorescence quenching by 1 mM sulphur dioxide in methanol. Fluorophore concentration in each case was 1uM.

Fluorophore	wavelength nm exci	fluo	% quenching	I_o/I
benzopurpurin	465	681	61.4	2.63
chloropyridine hydrochloride	256	574	53.84	2.16
hydrazine HCl	307	418	22.5	1.3
new fuchsin	550	669	100	—
CDF	471	538	80.4	5.1

Table-1 shows the effect of 1 mM SO_2 on the fluorescence intensity of several indicators, which were found sensitive to SO_2. Fluorescein showed interferences from other gases. New fuschin fluorescence is not quenched, but rather reduced because of a ground state chemical reaction. Hydrazine hydrochloride and chloropyridine hydrochloride do not have visible excitation and therefore were not considered for further investigations.

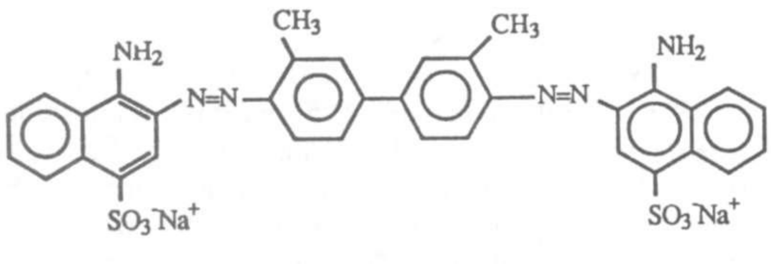

Figure 1. Chemical structure of benzopurpurin 4B.

The chemical structure of benzopurpurin 4B is shown in fig. 1. Stern-Volmer plot for the quenching of benzopurpurin by SO_2 is given in fig. 2. The data were collected with intensity monitored at the fluorescence maxim ca. 681 nm and the dye excited at 465 nm. It is obvious from the linearity of this plot that, within the concentration range investigated, fluorescence quenching by SO_2 strictly obeys the Stern-

Volmer relation:

$$I_o/I = 1 + K_{SV}[SO_2] \quad (1)$$

where I_o and I are, respectively, the fluorescence intensities of the fluorophore in the absence and presence of quencher concentration $[SO_2]$. K_{SV} is the Stern-Volmer constant.

SO_2 was found to be a very efficient quencher of the fluorescence of BP, having a Stern-Volmer quenching constant of 1493 M^{-1}. This is 5 times higher than which was observed in the case of fluoranthane[2]. The observed high efficiency of fluorescence quenching indicates that a process other than dynamic quenching is operative in this case.

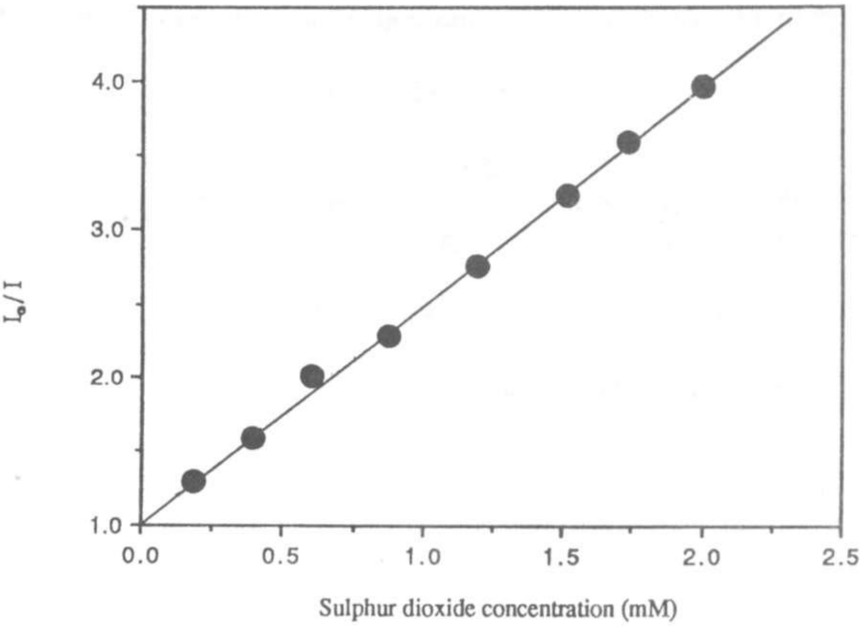

Figure 2. Stern-Volmer plots of the quenching of benzopurpurin 4B by SO_2 in methanol.

In a separate experiment, the absorption spectra of 15 μM BP was recorded both in the presence and absence of SO_2. No difference was observed in the two cases. This ruled out the possibilities of a ground state interaction between BP and SO_2. We think that an excited state charge transfer between benzopurpurin and SO_2 is the principal mechanism responsible for the observed fluorescence quenching.

The finding that SO_2 is an extremely efficient quencher of the fluorescence of BP can be used for the measurements of SO_2 in industrial and environmental applications. The possibility of making SO_2 measurements in air is of particular interest. The measurement of BP fluorescence, and consequently the quenching of this fluorescence by SO_2, is possible. This is especially attractive, since other major pollutant gases, such as H_2S and NH_3 do not interfere in the measurement. A simple device to monitor SO_2 dissolved in liquids/gases, based on fluorescence quenching of BP is possible. Optical properties of BP are well suited for the use of simple, inexpensive and durable solid state optoelectronic components. In addition, the broad features of the excitation and emission spectra provide a great deal of flexibility in designing the optics for a particular application. These features suggest that a compact and inexpensive instrumentation can be readily developed for SO_2 measurements based on BP fluorescence quenching.

4. CONCLUSIONS

The finding that SO_2 quenches selectively and extremely efficiently the fluorescence of benzopurpurin has several significant analytical applications, including (a) the direct fluorometric determination of SO_2, using the Stern-Volmer plot as a calibration curve, favourably in combination with flow injection analysis, (b) direct fluorometric titration of SO_2, using benzopurpurin as an end point indicator, (c) development of and improved waveguide sulphur dioxide sensors/detector and (d) possibilities of developing an improved fibre optic sensor/probe for the measurement of SO_2. Development of one such device is in advanced stages.

5. ACKNOWLEDGMENTS

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6. REFERENCES

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Note: Benzopurpurin 4B has shown concentration dependent spectral shifts and this behaviour is being investigated.